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ISO/TC 183/WG 2A - DETERMINATION OF SILVER IN COPPER CONCENTRATES STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA 1984-1986

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Analytical Methodology

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ISO/TC 183/WG 2A - DETERMINATION OF SILVER IN COPPER CONCENTRATES STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA 1984-1986

by

R. Sutarno* and W.S. Bowman**

SUMMARY

The analytical data resulting from the international test on the determination of Ag in copper concentrates by fire assay - A.A.S. method conducted by ISO/TC 183/WG 2A during the period of 1984-1986 have been statistically evaluated. Based on these analytical results, the precision of the analytical method can be expressed in terms of the Ag concentration level by the following equations:

$r = 0.0243\ X + 0.6012$

$P = 0.0461\ X + 4.3690$

$\sigma_r = 0.0086\ X + 0.2124$

$\sigma_L = 0.0151\ X + 1.5605$

where X is the Ag concentration in the sample, r is the repeatability, P is the permissible tolerance, σ_r is the within-laboratory standard deviation and σ_L is the between-laboratories standard deviation all in µg/g. Six samples containing Ag ranging from 30 to 1500 µg/g were used in this international test.

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ISO/CT 183/WG 2A - DÉTERMINATION DE LA TENEUR EN ARGENT DES CONCENTRÉS DE CUIVRE ÉVALUATION STATISTIQUE DES DONNÉES RECUEILLIES LORS DE L'ESSAI À L'ÉCHELLE INTERNATIONALE (1984-1986)

par

R. Sutarno* et W.S. Bowman**

RÉSUMÉ

Les données analytiques recueillies lors d'un essai à l'échelle internationale visant à déterminer la teneur en argent des concentrés de cuivre au moyen d'un essai pyrognostique en utilisant la méthode A.A.S., mené par l'ISO/CT 183/WG 2A au cours de la période allant de 1984-1986 ont fait l'objet d'une évaluation statistique. D'après les résultats de l'analyse statistique des données, la précision de la méthode analytique peut être exprimée en fonction du niveau de concentration de l'argent par les équations suivantes:

$r = 0.0243\ X + 0.6012$

$P = 0.0461\ X + 4.3690$

$\sigma_r = 0.0086\ X + 0.2124$

$\sigma_L = 0.0151\ X + 1.5605$

où X = la concentration en argent de l'échantillon, r = la répétabilité, P = l'écart admissible, σ_r = l'écart type en laboratoire et σ_L = l'écart type interlaboratoire (tous en ug/g). Six échantillons contenant de 30 à 1 500 µg/g d'argent ont été utilisés au cours de l'essai à l'echelle international.

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INTRODUCTION

The analytical data were collected by the convener of ISO/TC 183/WG 2A (Technical Committee 183 - Copper, Lead and Zinc Ores and Concentrates, Working Group 2A - Silver in Copper Concentrates) from an international test conducted during the period of 1984-1986. Six samples of copper concentrates with silver contents ranging from 30 to 1500 µg/g were used. Seventeen laboratories provided analytical data; each analysed the sample in triplicate.

The purpose of this statistical evaluation is to provide the working group with the preliminary estimates of the precision in the form of repeatability, permissible tolerance, and witnin-laboratory and between-laboratories standard deviation.

PRINCIPLE OF ANALYTICAL METHOD (1)

Fuse the sample using the prescribed fluxing reagent and procedure to obtain a correct weight of lead button.

The lead button from a fire assay fusion of a test portion is scorified to produce a lead button of mass, 2 to 3 g.

Retreatment fusion of the primary fusion and scorification slags to produce a low silver content lead button which is scorified to approximately 2 to 3 g.

Both lead buttons are dissolved in dilute nitric acid and the solution diluted to 500 mL.

Silver is determined in this solution by atomic absorption spectrometry using standards with matching lead concentration.

All values are reported on dry basis (2).

STATISTICAL EVALUATION

The analytical data were statistically evaluated by the procedure described in document ISO/TC 102/TCR 5 (3). Because each participating laboratory analysed only one bottle of each sample, as required by WG stage

A, the two-way analysis of variance (ANOVA) part of the procedure was by-passed. No confirmation of sample homogeneity was made; thus the between-laboratory variance may include, if any, the between-bottles variation of the sample. This procedure is illusrated schematically in Figure 1.

The raw data and the detailed calculations are presented in Appendix A. They are summarized in Tables 1 and 2. The raw data are also plotted in Figure 2. The boxed points in these figures signify that the data were suspected outliers and were excluded from the estimation of the sample means and the precisions. The letter C on the boxed data signifies that these data were suspected to be outliers due to poor precision (Cochran's test) and the letter D signifies deviation from the sample mean (Dixon's test).

The precisions estimated (σ_r, σ_L, r and P) are plotted against these corresponding sample means in Figure 3, and the regression equations of these precisions versus sample means were computed and presented in Table 1.

OBSERVATION

An ideal standard analytical method is an analytical method that can be applied by any qualified analyst with proper equipment and reagents to produce results with high precision and accuracy. This implies that the better the method is standardized, the smaller the variation between laboratories, i.e. the smaller the σ_L/σ_r ratio, and the fewer the outliers. The magnitude of the within-laboratory precision (σ_r) depends on the stage of the art of the method and also depends on the requirement imposed by the intended use of the standard method. Experience from other similar work has shown that on average $\sigma_L/\sigma_r = 2$ is considered reasonable for a good method.

Table 1 shows that both the magnitude of σ_r and the σ_L/σ_r ratio seem to be reasonable with the exception of sample 85-2. For some reason the analytical results for this sample gives an unrealistically low σ_r and consequently high σ_L/σ_r ratio. Furthermore, Table 2 shows that four laboratories had difficulties analysing this sample.

REFERENCES

1. "Copper, lead and zinc ores and concentrates - Determination of silver by fire assay - A.A.S. method"; First working draft, ISO/TC 183 (WG 2A-1), April 1985.

2. "Copper, lead and zinc ores and concentrates - Determination of hygroscophic moisture in the analysis sample"; First working draft, ISO/TC 183 N 90 E, 1985-03-28.

3. "Procedure for statistical evaluation of analytical data resulting from international tests"; ISO/TC 102/TCR 5, 1985-06-11.

Abbreviations Used in this Report

σ_r = SIGMA-R - within laboratory standard deviation

σ_L = SIGMA-L - between laboratories standard deviation

r* = R - repeatability

= $2.83\ \sigma_r$

p** = permissible tolerance between laboratories

= $2.83\left(\sigma_L^2 + \sigma_r^2/2\right)^{\frac{1}{2}}$

* Repeatability, r, is the value below which the absolute difference between two independent single test (analysis) results produced by a laboratory on identical material using the same equipment within a short interval of time, using the standardized test method, may be expected to be with a 95% probability.

** Permissible tolerance between laboratories, P, is the value below which the absolute difference between two means of duplicate test results on identical material obtained by operators of different laboratories using the standardized test method, may be expected to lie with a 95% probability.

KO - total number of participating laboratories

K - number of sets of laboratory results used for ANOVA

NO - total number of analytical results

N - No. of analytical results used for ANOVA

AU = Australia
BR = Brazil
CHN = China
CND = Canada
CZ = Czechoslovakia
FR = France
GER = Germany
HGR = Hungary
IND = India
IT = Italy
JP = Japan
NL = Netherlands
NZ = New Zealand
PHL = Philippines
PNG = Papua New Guinea
POL = Poland
SA = South Africa
SW = Sweden
UK = United Kingdom
USA = United States
USS = Soviet Union
YU = Yugoslavia

Table 1

ISO/TC 183/WG 2A/WG 2A-9 SILVER IN COPPER CONC. BY FA-AAS METHOD

SUMMARY OF PRECISIONS FOR ALL SAMPLES

ELEMENT	SAMPLE	KO	K	NO	N	MEAN(X) ug/g	REPEATABILITY ug/g	PERMISSIBLE TOLERANCE ug/g	SIGMA-R ug/g	SIGMA-L ug/g	SIGMA-L/SIGMA-R ug/g
SILVER	89-1	17	17	51	51	76.9667	5.0975	10.1242	1.80125	3.34305	1.86
SILVER	89-2	17	13	51	39	179.6769	2.4437	10.0919	.86351	3.79976	4.40
SILVER	89-3	15	15	45	45	957.0289	9.3897	27.2181	3.30024	9.33029	2.83
SILVER	89-4	16	15	48	45	141.5044	4.4994	11.6211	1.58990	3.94949	2.48
SILVER	89-9	16	15	48	45	28.4996	3.7302	6.2913	1.31808	2.01825	1.53
SILVER	89-11	15	14	45	42	1966.0119	40.3978	77.5364	14.27499	24.47088	1.78

THE REGRESSION EQUATIONS ARE:

			CORR. COEFF.
R	=	.0243 X + .6012	.9785
P	=	.0461 X + 4.3690	.9976
SIGMA-R	=	.0086 X + .2124	.9785
SIGMA-L	=	.0181 X + 1.3605	.9986

Table 2

ISO/TC 183/WG 2A/WG 2A-9 SILVER IN COPPER CONC. BY FA-AAS METHOD

LIST OF OUTLIERS

ELEMENT	SAMPLE	COCHRAN (PRECISION)	DIXON (ACCURACY)	LAB HAS ONLY ONE RESULT	INDIVIDUAL OUTLYING RESULT (DIXON)
SILVER	89-1	-	-	-	-
SILVER	89-2	AU 1	AU 1	-	-
		AU 2	-	-	-
		CHN 1	-	-	-
		CHN 2	-	-	-
SILVER	89-3	-	-	-	-
SILVER	89-4	AU 1	-	-	-
SILVER	89-5	-	AU 1	-	-
SILVER	89-11	-	AU 2	-	-

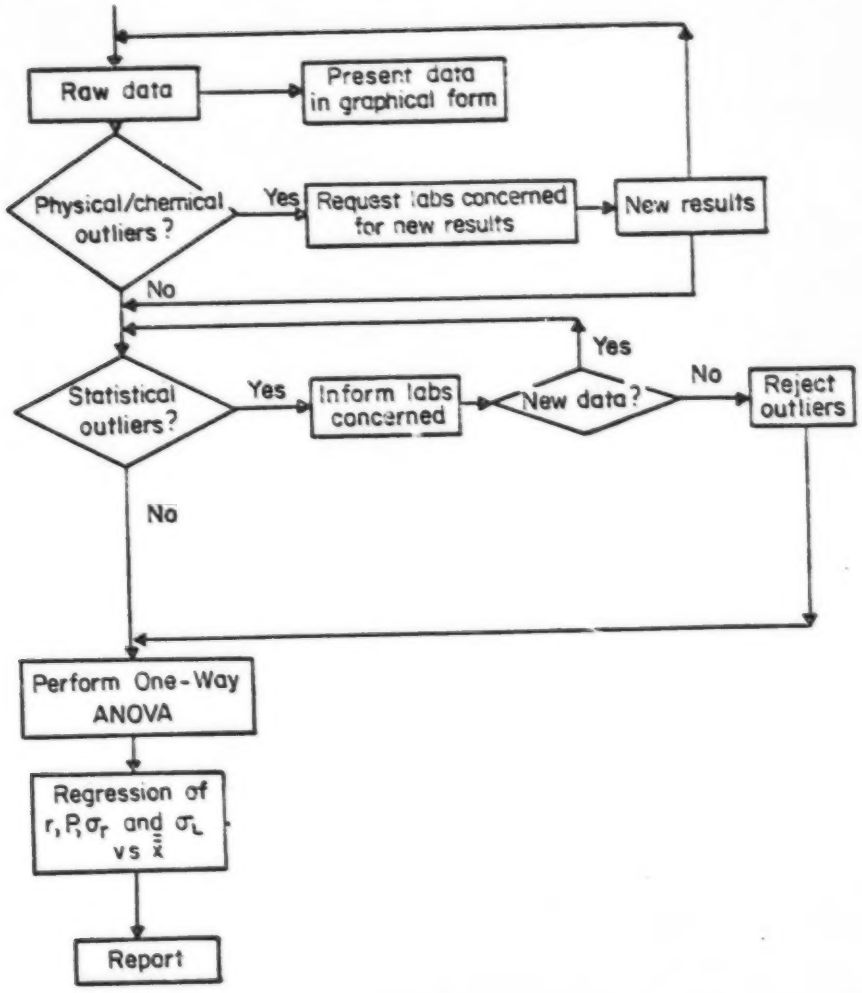
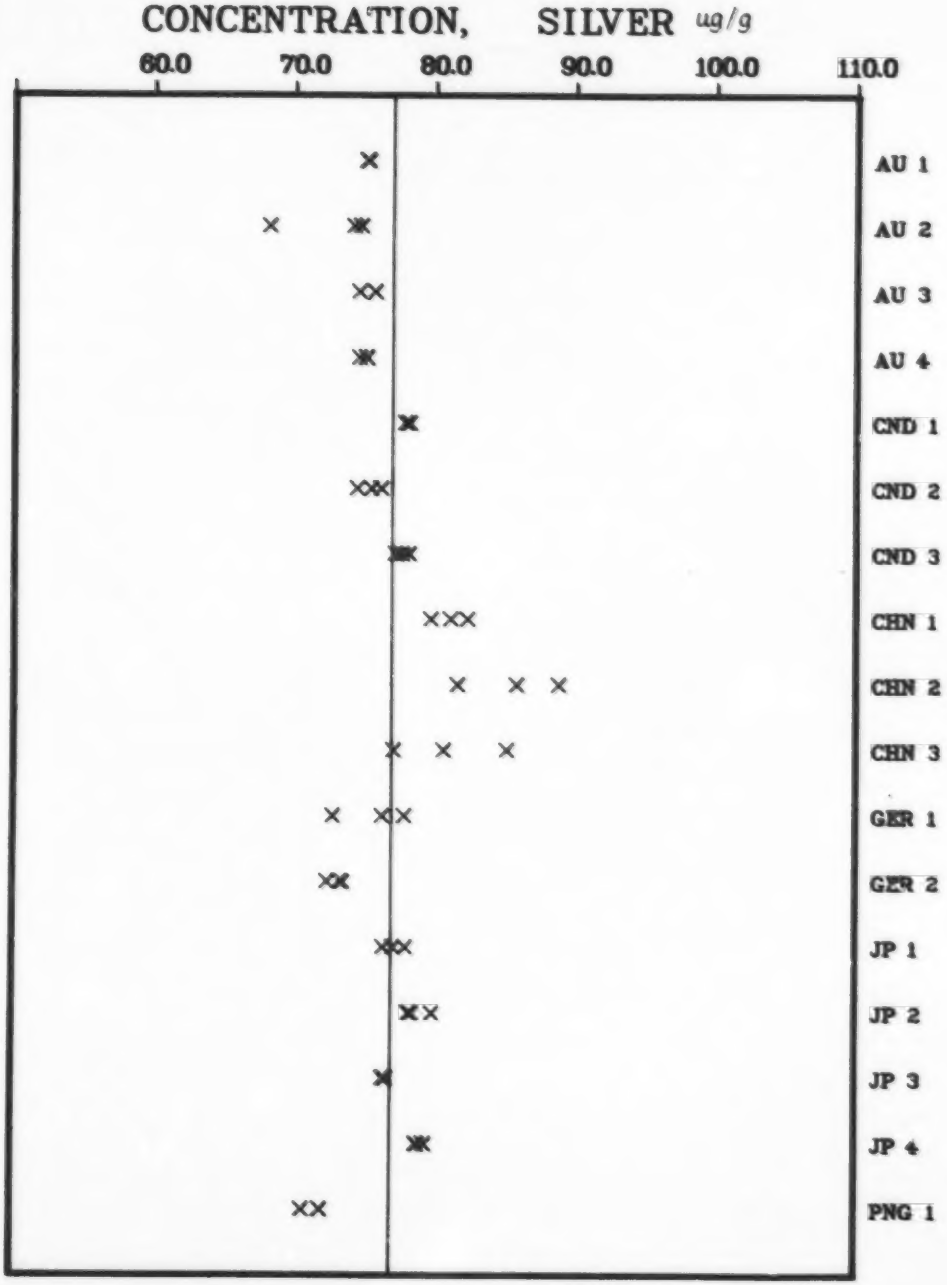
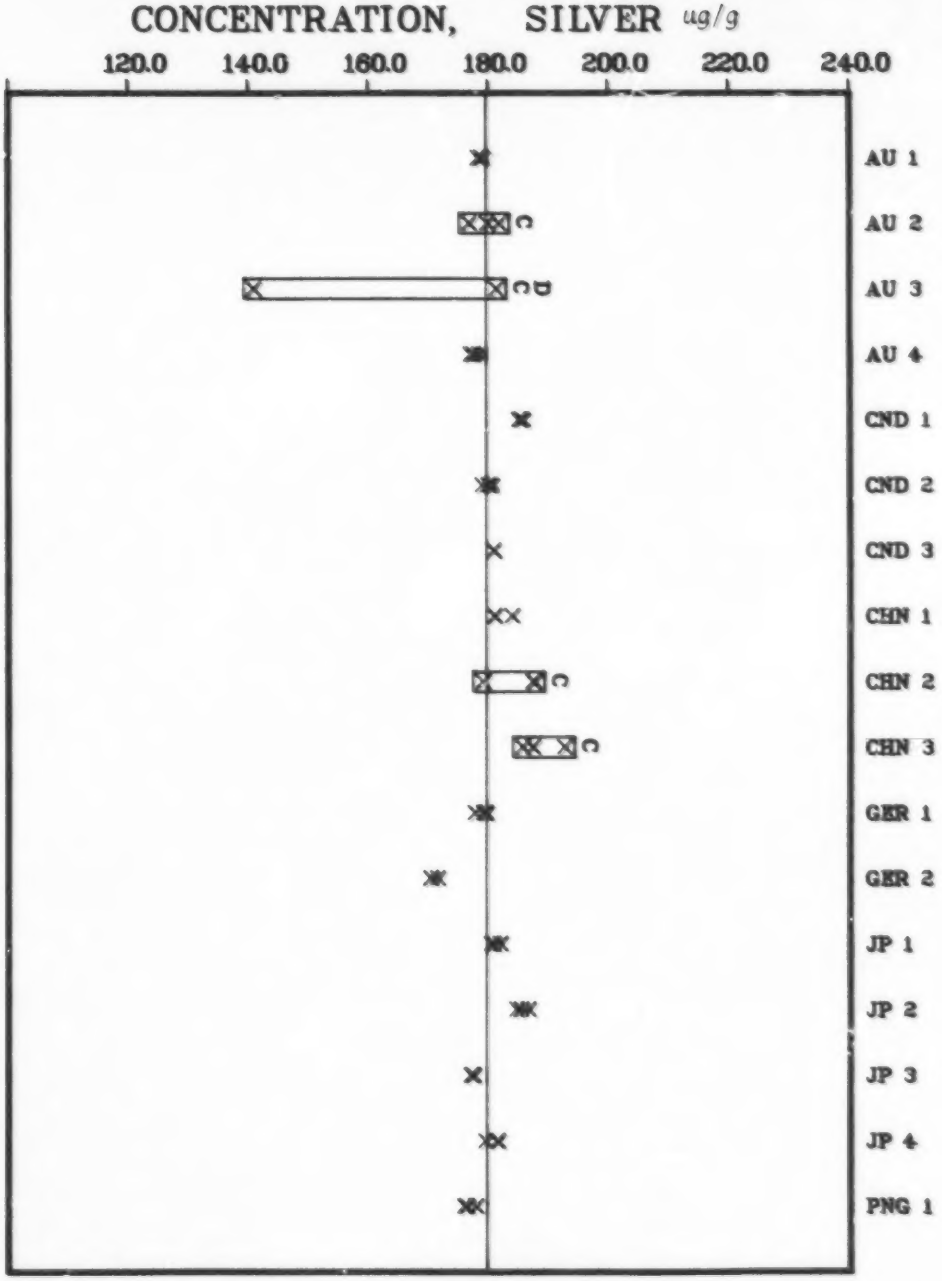


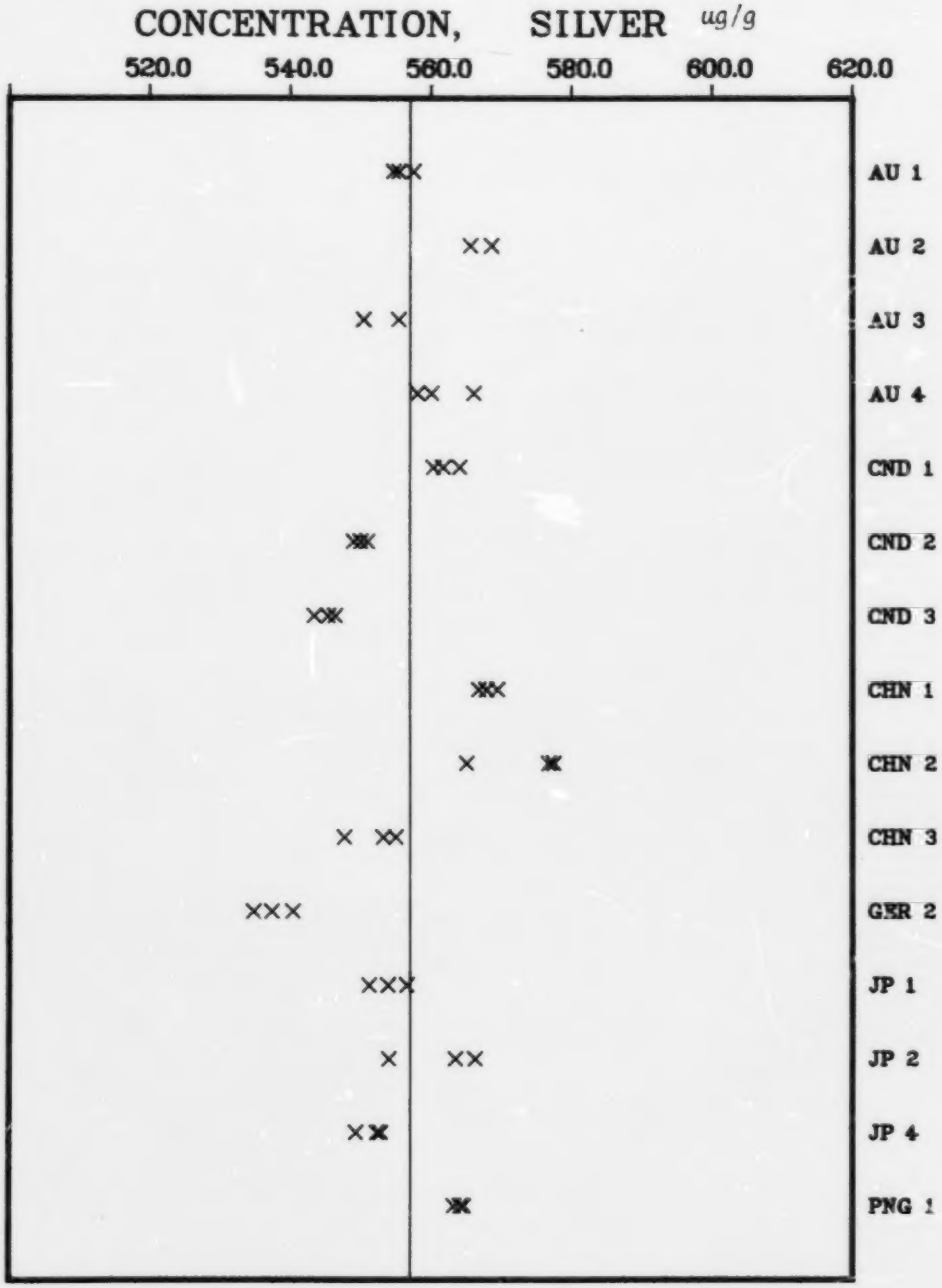
Figure 1. Flow Chart of the Procedure for Statistical Evaluation of Analytical Data Resulting from International Tests If The Test Sample is Known to be Homogeneous.



ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-1
Figure 2.1



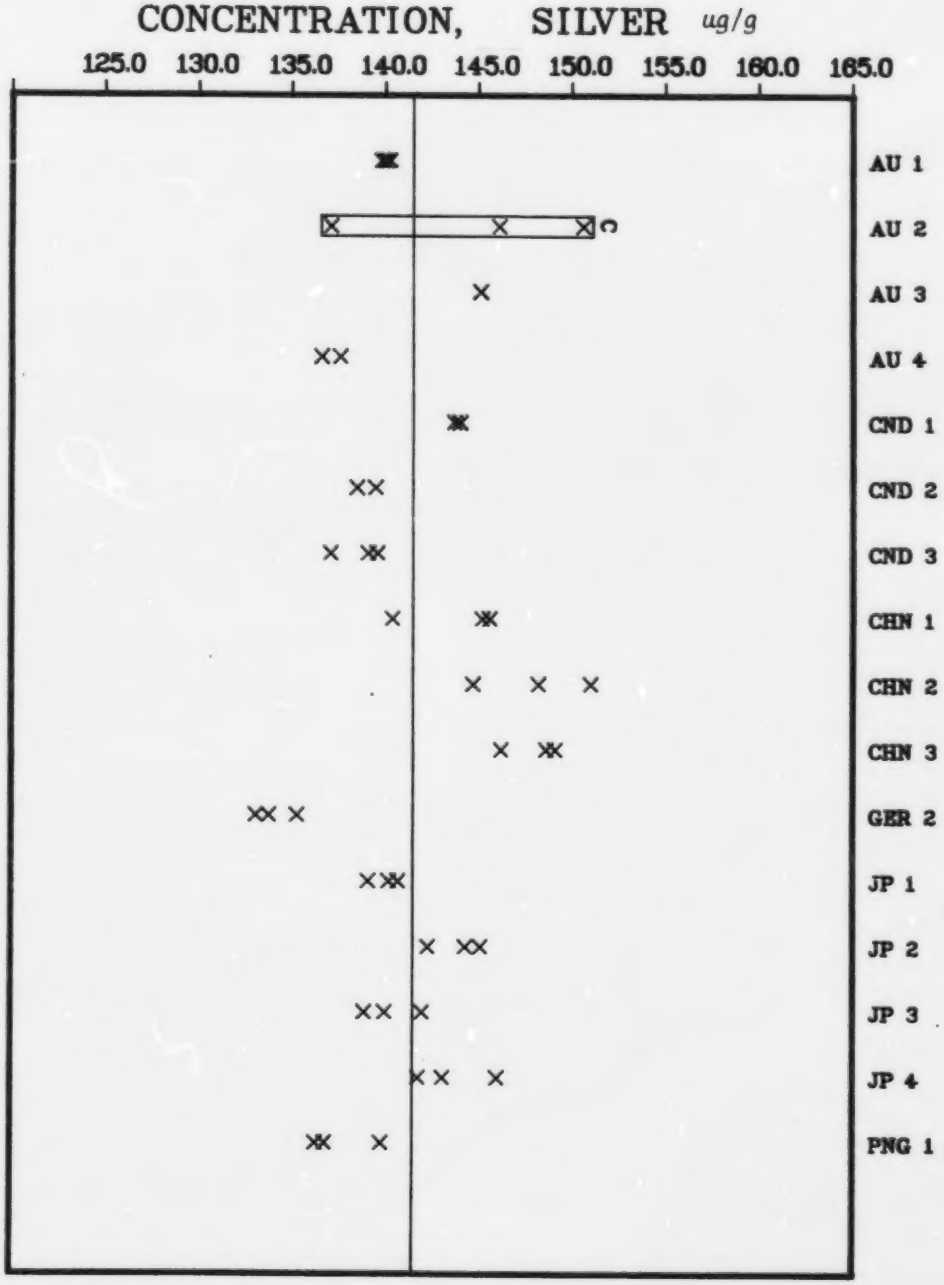
ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE 85-2
Figure 2.2



ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD

SAMPLE: 85-3

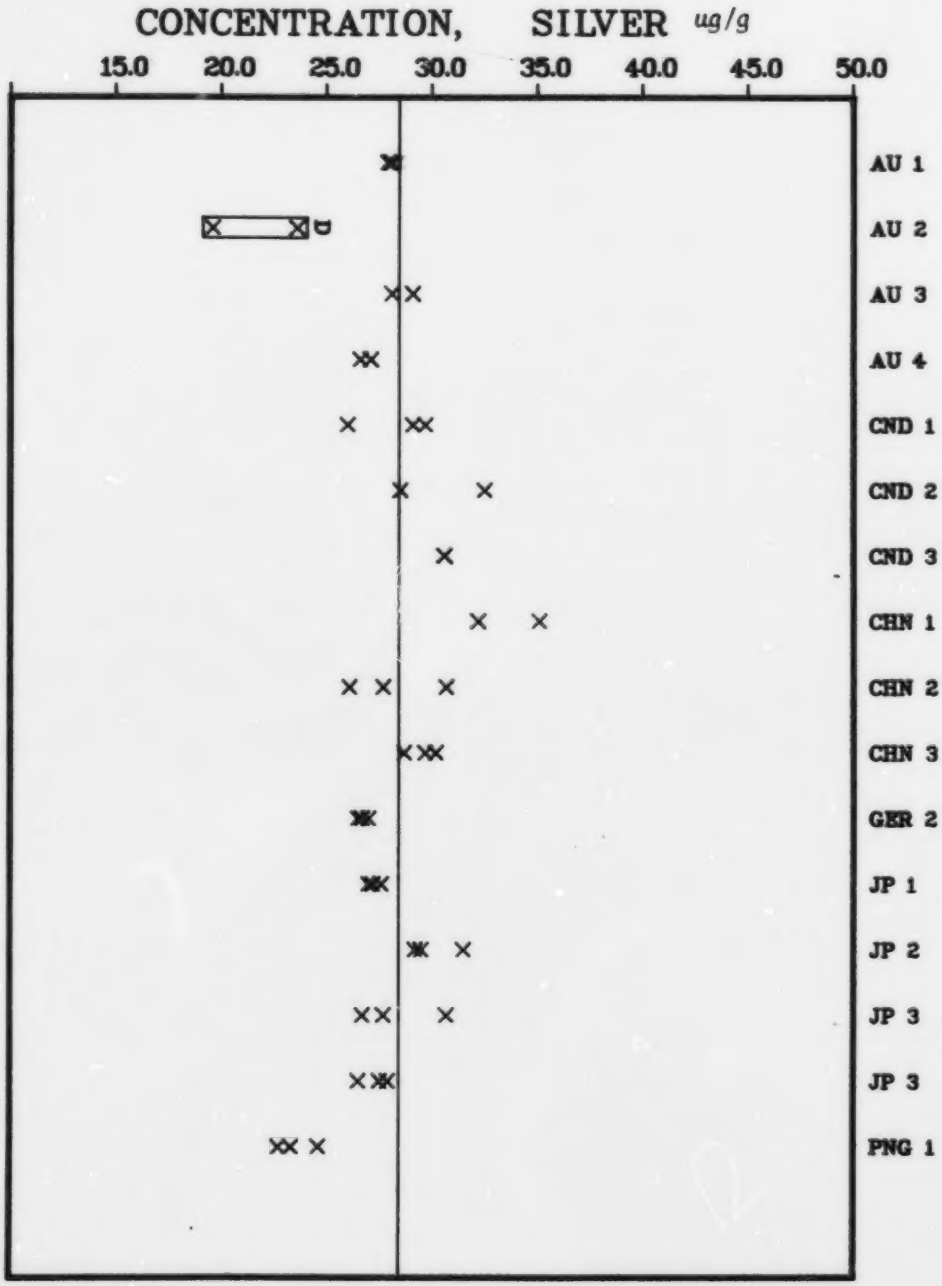
Figure 2.3



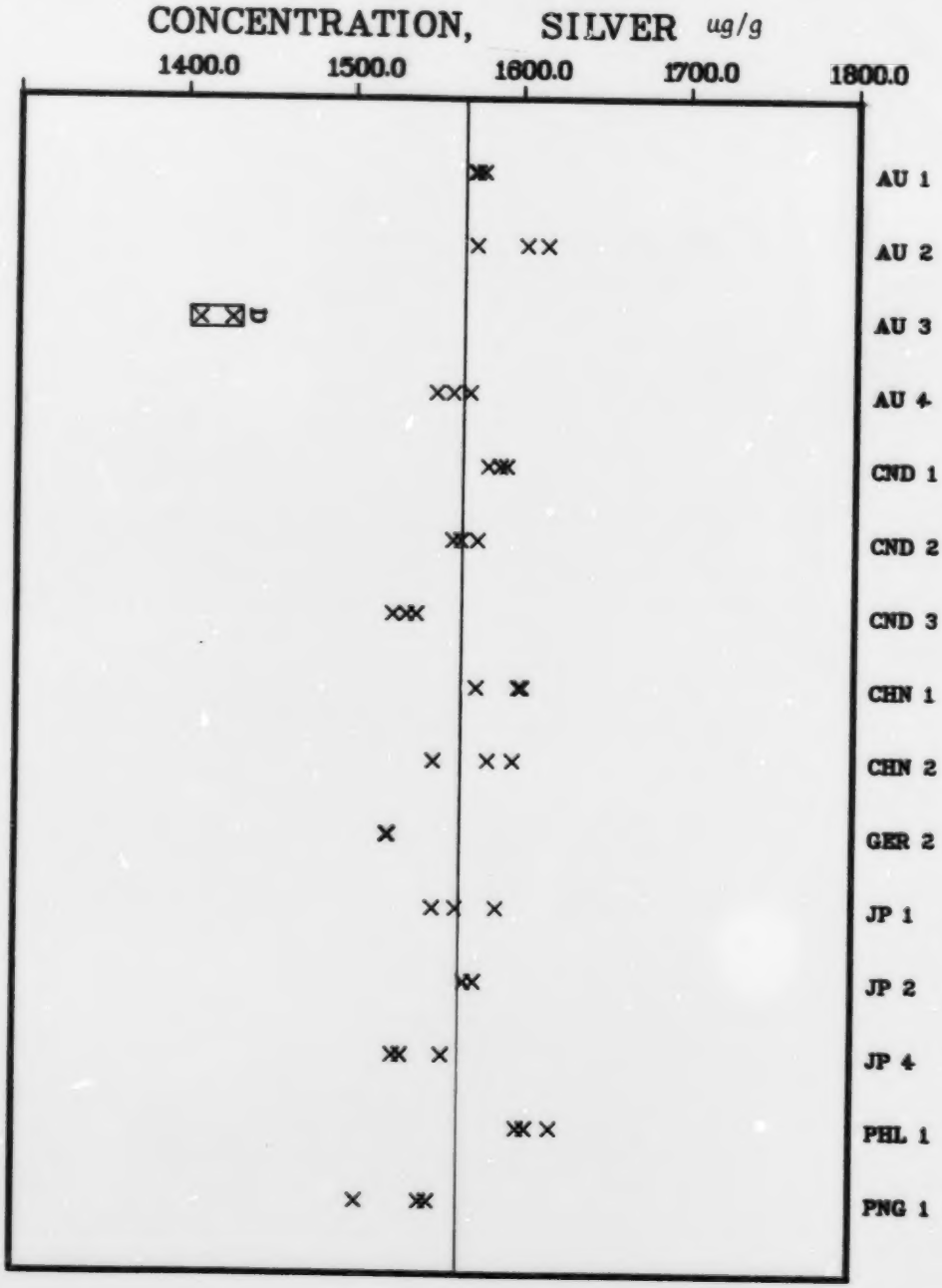
ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD

SAMPLE 85-4

Figure 2.4



ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-5
Figure 2.5



ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-11
Figure 2.6

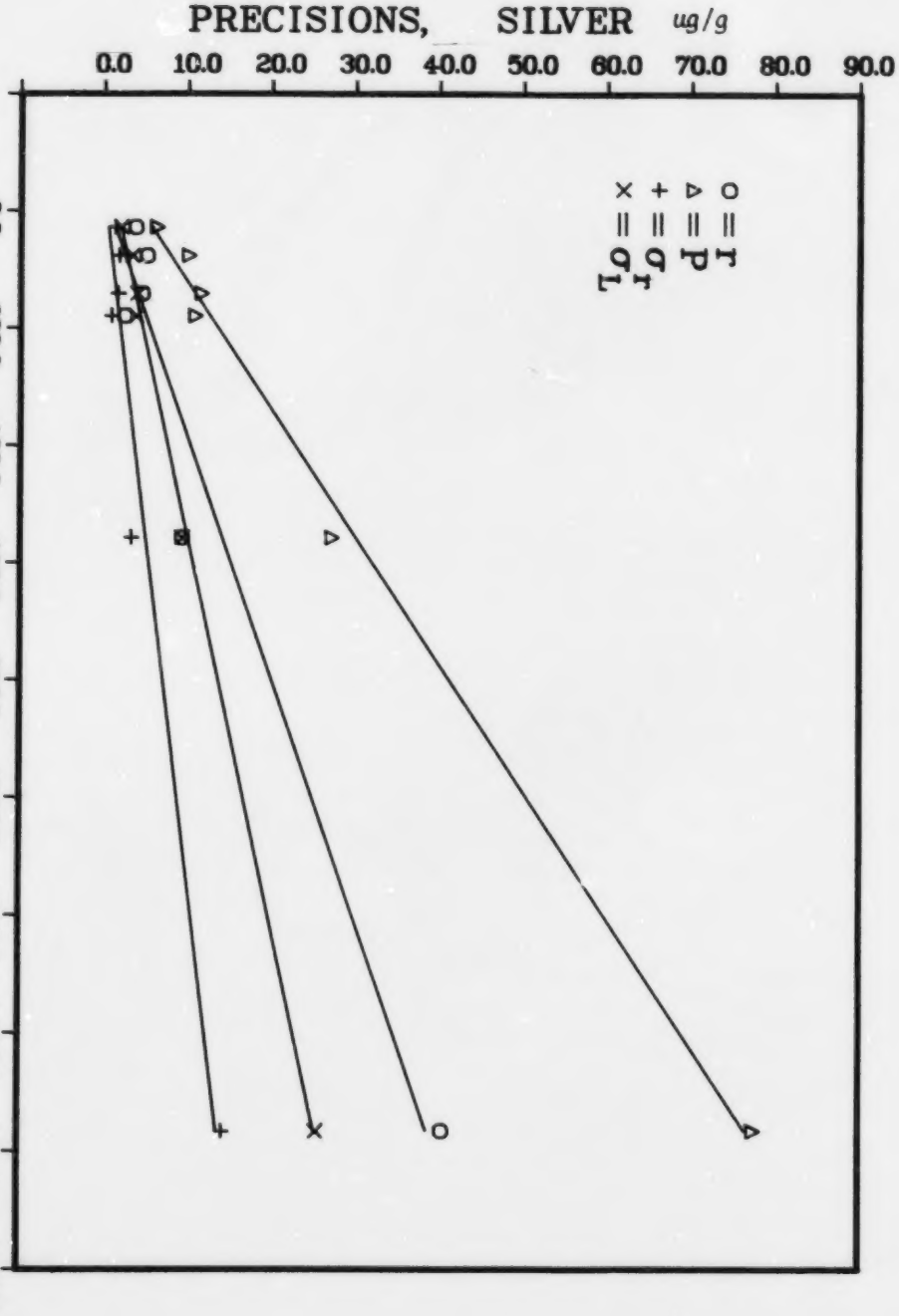


Figure 3 ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD

APPENDIX A

Silver in Copper Concentrates by FA-AAS Method
Detailed Computation of the Analytical Data

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-1

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS SILVER			LAB MEAN	LAB VARIANCE
1	AU 1	1	75.2000	75.1000	75.1000	75.13333	.3333E-02
2	AU 2	1	74.7000	74.2000	68.2000	72.36667	.1308E+02
3	AU 3	1	74.6000	75.7000	75.7000	75.33333	.4033E+00
4	AU 4	1	75.1000	75.1000	74.6000	74.93333	.8333E-01
5	CND 1	1	78.2000	77.9000	78.2000	78.10000	.3000E-01
6	CND 2	1	75.5000	74.5000	76.2000	75.40000	.7300E+00
7	CND 3	1	78.2000	77.7000	77.2000	77.70000	.2500E+00
8	CHN 1	1	79.8000	81.2000	82.4000	81.13333	.1693E+01
9	CHN 2	1	88.9000	81.7000	85.9000	85.50000	.1308E+02
10	CHN 3	1	77.1000	85.2000	80.7000	81.00000	.1647E+02
11	GER 1	1	76.3000	77.9000	72.8000	75.66667	.6803E+01
12	GER 2	1	72.4000	73.3000	73.5000	73.06667	.3433E+00
13	JP 1	1	78.0000	77.1000	76.4000	77.16667	.6433E+00
14	JP 2	1	78.2000	78.4000	79.9000	78.83333	.8633E+00
15	JP 3	1	76.4000	76.5000	76.6000	76.50000	.1000E-01
16	JP 4	1	78.9000	78.8000	79.4000	79.03333	.1033E+00
17	PNG 1	1	72.0000	70.7000	72.0000	71.56667	.5633E+00

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-1

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	56.152
CHI-SQUARE(.95,16)	26.301

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

NONE REJECTED

DIXON'S TEST FOR LABORATORY MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 89-1

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	16	.58836000E+03	.36772500E+02
WITHIN LABS	34	.11031333E+03	.32445098E+01
TOTAL	50	.69867333E+03	

REPEATABILITY VARIANCE	.32445098E+01
REPEATABILITY STD. DEV.	1.80125229
BETWEEN-LABORATORIES VARIANCE	.11175997E+02
BETWEEN-LABORATORIES STD. DEV.	3.34305201
REPEATABILITY	5.09754397
PERMISSIBLE TOLERANCE BETWEEN LABS	10.12422429
GRAND MEAN	76.96666667
VARIANCE OF THE GRAND MEAN	.72102941E+00

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-2

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS SILVER			LAB MEAN	LAB VARIANCE
1	AU 1	1	178.4000	179.0000	178.4000	178.60000	.1200E+00
2	AU 2	1	181.9000	176.9000	179.9000	179.56667	.6333E+01
3	AU 3	1	181.4000	141.0000	141.0000	154.46667	.5441E+03
4	AU 4	1	177.1000	178.6000	177.6000	177.76667	.5833E+00
5	CND 1	1	185.1000	185.3000	185.7000	185.36667	.9333E-01
6	CND 2	1	179.0000	180.5000	180.0000	179.83333	.5833E+00
7	CND 3	1	180.9000	180.9000	180.9000	180.90000	.4657E-09
8	CHN 1	1	181.0000	181.1000	184.0000	182.03333	.2903E+01
9	CHN 2	1	179.1000	187.7000	187.4000	184.73333	.2382E+02
10	CHN 3	1	185.7000	192.7000	187.4000	188.60000	.1333E+02
11	GER 1	1	179.2000	179.6000	177.8000	178.86667	.8933E+00
12	GER 2	1	171.6000	170.5000	170.4000	170.83333	.4433E+00
13	JP 1	1	180.4000	182.0000	180.9000	181.10000	.6700E+00
14	JP 2	1	186.7000	185.5000	184.7000	185.63333	.1013E+01
15	JP 3	1	177.1000	177.5000	177.2000	177.26667	.4333E-01
16	JP 4	1	181.4000	179.5000	181.6000	180.83333	.1343E+01
17	PNG 1	1	176.0000	177.9000	176.4000	176.76667	.1003E+01

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 89-2

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	130.465
CHI-SQUARE(.95,16)	26.301

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

LAB- 3	C-CALC =	.911	C-CRIT(3,17) =	.305
LAB- 9	C-CALC =	.448	C-CRIT(3,16) =	.319
LAB-10	C-CALC =	.454	C-CRIT(3,15) =	.334
LAB- 2	C-CALC =	.395	C-CRIT(3,14) =	.351

DIXON'S TEST FOR LABORATORY MEANS

LAB- 3	R =	.722	D-CRIT(17) =	.530

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 2	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB- 3	DIXON'S TEST FOR MEANS AND COCHRAN'S TEST FOR VARIANCE
LAB- 9	COCHRAN'S TEST FOR LABORATORY VARIANCE
LAB-10	COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-2

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	12	.52872256E+03	.44060214E+02
WITHIN LABS	26	.19386667E+02	.74564103E+00
TOTAL	38	.54810923E+03	

REPEATABILITY VARIANCE	.74564103E+00
REPEATABILITY STD. DEV.	.86350508
BETWEEN-LABORATORIES VARIANCE	.14438191E+02
BETWEEN-LABORATORIES STD. DEV.	3.79976195
REPEATABILITY	2.44371938
PERMISSIBLE TOLERANCE BETWEEN LABS	10.89127675
GRAND MEAN	179.67692308
VARIANCE OF THE GRAND MEAN	.11297491E+01

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-3

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS SILVER			LAB MEAN	LAB VARIANCE
1	AU 1	1	555.4000	554.6000	557.5000	555.83333	.2243E+01
2	AU 2	1	565.6000	568.6000	568.6000	567.60000	.3000E+01
3	AU 3	1	550.4000	550.4000	555.4000	552.06667	.8333E+01
4	AU 4	1	566.1000	558.1000	560.1000	561.43333	.1733E+02
5	CND 1	1	560.4000	561.8000	564.1000	562.10000	.3490E+01
6	CND 2	1	551.0000	549.0000	550.0000	550.00000	.1000E+01
7	CND 3	1	546.4000	543.4000	545.4000	545.06667	.2333E+01
8	CHN 1	1	569.5000	567.9000	566.8000	568.06667	.1843E+01
9	CHN 2	1	565.1000	576.8000	577.5000	573.13333	.4852E+02
10	CHN 3	1	547.7000	553.2000	555.0000	551.96667	.1446E+02
11	GER 2	1	537.4000	540.4000	534.8000	537.53333	.7853E+01
12	JP 1	1	553.9000	551.2000	556.6000	553.90000	.7290E+01
13	JP 2	1	554.0000	566.3000	563.5000	561.26667	.4156E+02
14	JP 4	1	552.3000	549.3000	552.8000	551.46667	.3583E+01
15	PNG 1	1	564.2000	563.2000	564.6000	564.00000	.5200E+00

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-3

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	19.156
CHI-SQUARE(.95,14)	23.691

VARIANCE IS HOMOGENEOUS

DIXON'S TEST FOR LABORATORY MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-3

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	14	.38087658E+04	.27205470E+03
WITHIN LABS	30	.32674667E+03	.10891556E+02
TOTAL	44	.41355124E+04	

REPEATABILITY VARIANCE	.10891556E+02
REPEATABILITY STD. DEV.	3.30023568
BETWEEN-LABORATORIES VARIANCE	.87054381E+02
BETWEEN-LABORATORIES STD. DEV.	9.33029372
REPEATABILITY	9.33966698
PERMISSIBLE TOLERANCE BETWEEN LABS	27.21809180
GRAND MEAN	557.02888889
VARIANCE OF THE GRAND MEAN	.60456600E+01

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-4

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS SILVER			LAB MEAN	LAB VARIANCE
1	AU 1	1	140.2000	139.8000	140.0000	140.00000	.4000E-01
2	AU 2	1	150.6000	137.1000	146.1000	144.60000	.4725E+02
3	AU 3	1	145.1000	145.1000	145.1000	145.10000	0.
4	AU 4	1	136.6000	136.6000	137.6000	136.93333	.3333E+00
5	CND 1	1	144.0000	144.0000	143.7000	143.90000	.3000E-01
6	CND 2	1	138.5000	138.5000	139.5000	138.83333	.3333E+00
7	CND 3	1	139.6000	139.1000	137.1000	138.60000	.1750E+01
8	CHN 1	1	145.2000	145.6000	140.4000	143.73333	.8373E+01
9	CHN 2	1	148.2000	144.7000	151.0000	147.96667	.9963E+01
10	CHN 3	1	146.2000	149.1000	148.6000	147.96667	.2403E+01
11	GER 2	1	133.1000	135.3000	133.8000	134.06667	.1263E+01
12	JP 1	1	140.7000	139.1000	140.2000	140.00000	.6700E+00
13	JP 2	1	144.3000	142.3000	145.1000	143.90000	.2080E+01
14	JP 3	1	142.0000	138.9000	140.0000	140.30000	.2470E+01
15	JP 4	1	146.0000	143.1000	141.8000	143.63333	.4623E+01
16	PNG 1	1	136.8000	139.8000	136.3000	137.63333	.3583E+01

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-4

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	35.623
CHI-SQUARE(.95,14)	23.691

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

LAB- 2 C-CALC = .555 C-CRIT(3,15) = .334

DIXON'S TEST FOR LABORATORY MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 2 COCHRAN'S TEST FOR LABORATORY VARIANCE

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-4

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	14	.69052578E+03	.49323270E+02
WITHIN LABS	30	.75833333E+02	.25277778E+01
TOTAL	44	.76635911E+03	

REPEATABILITY VARIANCE	.25277778E+01
REPEATABILITY STD. DEV.	1.58989867
BETWEEN-LABORATORIES VARIANCE	.15598497E+02
BETWEEN-LABORATORIES STD. DEV.	3.94949330
REPEATABILITY	4.49941323
PERMISSIBLE TOLERANCE BETWEEN LABS	11.62106558
GRAND MEAN	141.50444444
VARIANCE OF THE GRAND MEAN	.10960727E+01

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-5

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS SILVER			LAB MEAN	LAB VARIANCE
1	AU 1	1	27.9000	28.0000	28.1000	28.00000	.1000E-01
2	AU 2	1	23.6000	19.6000	23.6000	22.26667	.5333E+01
3	AU 3	1	28.1000	29.1000	29.1000	28.76667	.3333E+00
4	AU 4	1	26.6000	27.1000	27.1000	26.93333	.8333E-01
5	CND 1	1	29.7000	26.0000	29.1000	28.26667	.3943E+01
6	CND 2	1	32.5000	28.5000	28.5000	29.83333	.5333E+01
7	CND 3	1	30.6000	30.6000	30.6000	30.60000	.1455E-10
8	CHN 1	1	32.2000	35.1000	32.2000	33.16667	.2803E+01
9	CHN 2	1	26.1000	30.7000	27.7000	28.16667	.5453E+01
10	CHN 3	1	29.7000	30.2000	28.7000	29.53333	.5833E+00
11	GER 2	1	27.0000	26.5000	26.7000	26.73333	.6333E-01
12	JP 1	1	27.6000	27.2000	27.0000	27.26667	.9333E-01
13	JP 2	1	29.5000	31.5000	29.2000	30.06667	.1563E+01
14	JP 3	1	26.7000	27.7000	30.7000	28.36667	.4333E+01
15	JP 3	1	27.9000	27.5000	26.5000	27.30000	.5200E+00
16	PNG 1	1	22.7000	23.3000	24.6000	23.53333	.9433E+00

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-5

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	69.576
CHI-SQUARE(.95,15)	25.000

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

NONE REJECTED

DIXON'S TEST FOR LABORATORY MEANS

LAB- 2 R = .573 D-CRIT(16) = .546

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 2 DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-5

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	14	.19540311E+03	.13957365E+02
WITHIN LABS	30	.52120000E+02	.17373333E+01
TOTAL	44	.24752311E+03	

REPEATABILITY VARIANCE	.17373333E+01
REPEATABILITY STD. DEV.	1.31807941
BETWEEN-LABORATORIES VARIANCE	.40733439E+01
BETWEEN-LABORATORIES STD. DEV.	2.01825269
REPEATABILITY	3.73016473
PERMISSIBLE TOLERANCE BETWEEN LABS	6.29126923
GRAND MEAN	28.43555556
VARIANCE OF THE GRAND MEAN	.31016367E+00

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-11

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS SILVER			LAB MEAN	LAB VARIANCE
1	AU 1	1	1572.9000	1571.3000	1576.9000	1573.70000	.8320E+01
2	AU 2	1	1615.3000	1572.8000	1602.8000	1596.96667	.4771E+03
3	AU 3	1	1408.1000	1427.1000	1427.1000	1420.76667	.1203E+03
4	AU 4	1	1569.7000	1549.6000	1559.6000	1559.63333	.1010E+03
5	CND 1	1	1592.0000	1581.0000	1588.0000	1587.00000	.3100E+02
6	CND 2	1	1565.0000	1560.0000	1575.0000	1566.66667	.5833E+02
7	CND 3	1	1538.4000	1532.4000	1524.4000	1531.73333	.4933E+02
8	CHN 1	1	1575.0000	1600.0000	1602.0000	1592.33333	.2263E+03
9	CHN 2	1	1582.0000	1597.0000	1549.2000	1576.06667	.5976E+03
10	GER 2	1	1522.3000	1521.8000	1521.4000	1521.83333	.2033E+00
11	JP 1	1	1549.6000	1563.5000	1588.1000	1567.06667	.3801E+03
12	JP 2	1	1569.1000	1569.1000	1575.3000	1571.16667	.1281E+02
13	JP 4	1	1531.4000	1526.3000	1555.9000	1537.86667	.2504E+03
14	PHL 1	1	1606.8000	1601.7000	1621.4000	1609.96667	.1045E+03
15	PNG 1	1	1543.2000	1548.2000	1505.1000	1532.16667	.5597E+03

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-11

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	25.545
CHI-SQUARE(.95,14)	23.691

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

NONE REJECTED

DIXON'S TEST FOR LABORATORY MEANS

LAB- 3 R = .647 D-CRIT(15) = .565

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 3 DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 183/WG 2A/WG 2A-3 SILVER IN COPPER CONC. BY FA-AAS METHOD
SAMPLE: 85-11

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	13	.27950884E+05	.21500680E+04
WITHIN LABS	28	.57055800E+04	.20377071E+03
TOTAL	41	.33656464E+05	

REPEATABILITY VARIANCE	.20377071E+03
REPEATABILITY STD. DEV.	14.27482799
BETWEEN-LABORATORIES VARIANCE	.64876576E+03
BETWEEN-LABORATORIES STD. DEV.	25.47088069
REPEATABILITY	40.39776322
PERMISSIBLE TOLERANCE BETWEEN LABS	77.53637699
GRAND MEAN	1566.01190476
VARIANCE OF THE GRAND MEAN	.51192095E+02